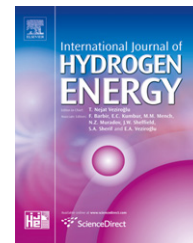


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A study on pulse plating amorphous Ni–Mo alloy coating used as HER cathode in alkaline medium

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ABSTRACT

The amorphous Ni–Mo film with high HER (hydrogen evolution reaction) activity was obtained by pulse plating. The optimum electrodeposition conditions with respect to HER overpotential were determined, e.g. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ concentration, current density and duty cycle. Correspondingly, the compositions and components of the Ni–Mo coatings with various molybdenum contents were investigated systematically. The results showed that when the ratio of nickel and molybdenum concentrations in the electrodeposition bath is lower than 1 (mol%), the molybdenum content in the coating decreases with the increasing $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ concentration, while the corresponding HER overpotential of the Ni–Mo film increases. The amorphous Ni–Mo coating was obtained when the molybdenum content was c.a. 30 mass%, which shows high HER activity ($\eta_{200} = 62$ mV at 200 mA cm^{-2} and 80°C) and excellent corrosion resistance. After galvanostatic electrolysis for 100 h in 33 mass% NaOH solution, the amorphous structure was destroyed due to the dissolution of molybdenum.

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1. Introduction

Hydrogen energy has been widely considered as substitution for fossil fuels in the future. Water electrolysis is a mature technology and it has been investigated for a long time, however, the high hydrogen evolution reaction overpotential restrains its large-scale application. In recent years, significant progress has been made in the field of preparing cathodic material [1–9]. Amongst these materials, the catalytic activity of Ni–Mo alloy electrode in the hydrogen evolution reaction is much higher than that of industrially applied nickel cathode, since the electron-transfer between

electron-rich Ni and electron-deficient Mo in the Ni–Mo alloy leads to a synergistic effect. Raj reported that the electrodeposited Ni–Mo coating was composed of MoNi_4 and MoO_3 phases, and the corresponding h.o.v. (hydrogen evolution overpotential) was 180 mV (1500 h) in 6 M KOH and 80°C under the current density 300 mA/cm^2 [10]. Huot reported that the Ni–Mo cathode synthesized by mechanical alloying technique is suitable for water electrolysis in view of its HER overpotential being 90 mV [11]. Rodríguez prepared the electro active Ni–Mo electrodes by mechanical alloying and pressure-less sintering Ni and Mo powders. The corresponding exchange current density for the hydrogen

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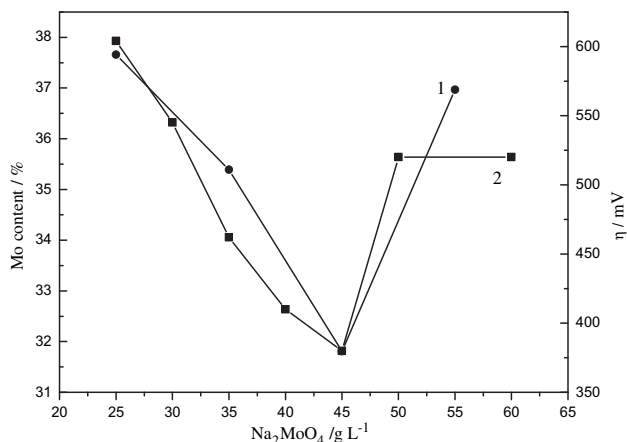


Fig. 1 – Impact of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ concentration on molybdenum contents and hydrogen evolution overpotentials of Ni–Mo coatings. 1 – Molybdenum contents of Ni–Mo coatings; 2 – Hydrogen evolution overpotentials of Ni–Mo coatings.

evolution reaction ranged from 27.3 to 1.4 mA/cm² [12]. Yagi reported that amorphous Ni–Mo alloy layers could be obtained at the surface of the nickel substrate by the alternating pulsed electrolysis using the MoO_4^{2-} solution of pH 3.0–5.0. The conditions for Ni–Mo alloy formation were discussed in terms of the dissolving regime of ionic species in the electrolytes determined by an equilibrium calculation [13]. Krstajic reported that the Ni–Mo alloy coating, which was electrodeposited from the pyrophosphate-sodium bicarbonate bath, possess high catalytic activity for hydrogen evolution in the NaOH solutions. However, low stability in the 33% NaOH at 85 °C was observed as a consequence of a deterioration of the alloy coatings [14].

Resulting from the “induced” co-deposition principle for Ni–Mo coating in galvanostatic plating process, hydrogen evolution process and concentration polarization will happen on the cathode significantly under high cathodic current density, which leads to rough surface of the obtained Ni–Mo coating with high internal stress and poor adhesive force. In comparison, since the concentration polarization could be

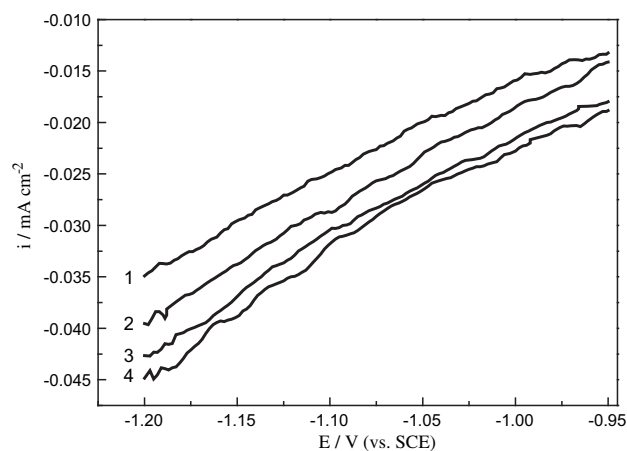


Fig. 2 – Bath polarization curves (The concentrations of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ increase from 10 to 40 g/L).

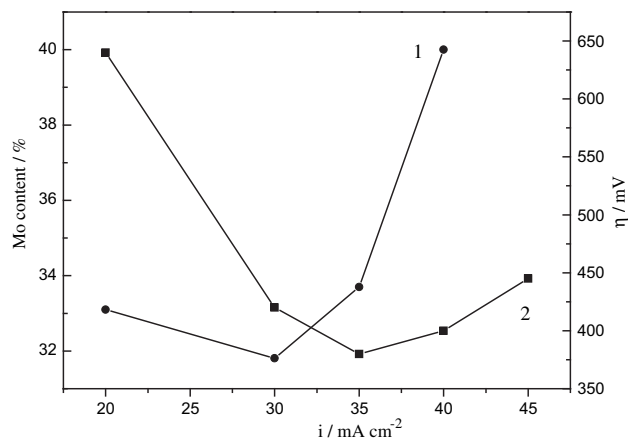


Fig. 3 – Impact of average cathodic current density on molybdenum contents and hydrogen evolution overpotentials of Ni–Mo coatings. 1 – Molybdenum content of Ni–Mo coatings; 2 – Hydrogen evolution overpotential of Ni–Mo coatings.

avoided, high cathodic current density is allowed in pulse plating process, and the formation speed of crystals could be faster than the galvanostatic plating process. Thus, uniform, smooth and dense coating could be obtained due to grain refinement. In this paper, Ni–Mo alloy was prepared by pulse plating, and the impacts of different electrodeposition conditions in pulse plating process on the composition, apparent morphology and HER activity of Ni–Mo coating were systematically investigated.

2. Experimental

Ni–Mo coatings were prepared by pulse plating method (pulse frequency being 500 Hz) using a modified Watts bath containing mainly 30 g/L $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 25–55 g/L $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 70 g/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ at 35 °C and pH = 8. HER overpotentials and the molybdenum content of the Ni–Mo alloy coating obtained as the indexes, the concentration of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$,

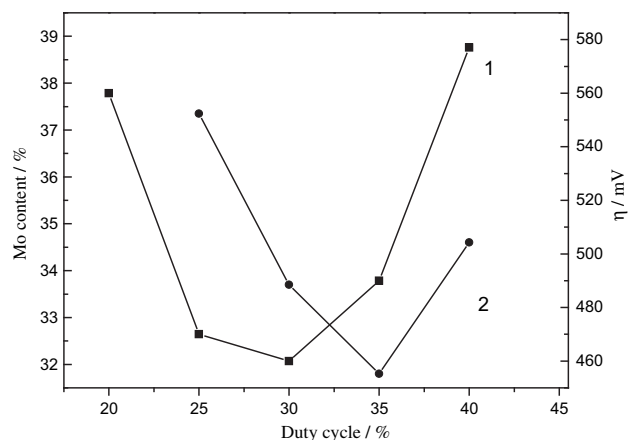


Fig. 4 – Impact of duty cycle on molybdenum contents and hydrogen evolution overpotentials of Ni–Mo coatings. 1 – Hydrogen evolution overpotential of Ni–Mo coatings; 2 – Molybdenum contents of Ni–Mo coatings.

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